The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

Editorial

"... Because of the low photosynthetic efficiency and the competition of energy plants with food plants for agricultural land, we should not grow plants for biofuel production ... "
Read more in the Editorial by Hartmut Michel.

Author Profile

"A good work day begins with an early morning workout at the gym.
My favorite song is "Supper's Ready" by Genesis. ..."
This and more about Michael M. Haley can be found on page 2540.

News

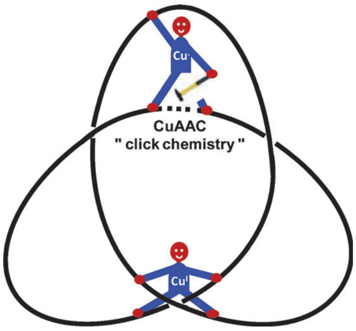
A. G. Doyle

S. E. Reisman

V. Köster

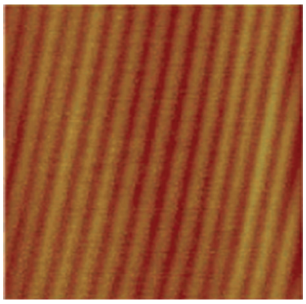
Books

Highlights



Collar and tie men: The smallest trefoil knot reported to date has been prepared by an active metal template synthesis. Copper(I) ions are able to constrain the well-designed structure so that it can form the loops by complexing to the bipyridine moieties in the core of the thread and the two ends of the entangled lace on opposite faces of the loop, before acting as a catalyst to close the lace (see picture).

Trefoil Knot

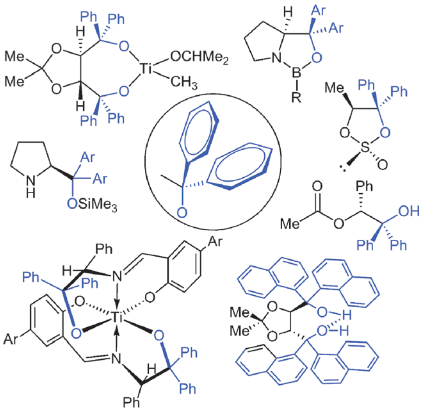


Not your cup of tea? "Coffee rings" of spherical colloidal particles are left behind after water droplets resting on surfaces have dried out. This controlled evaporation of colloidal solutions can be exploited to deposit material in regular patterns (see picture). It is now shown that if spherical colloids are replaced by slightly elongated ones, the coffee ring is not formed and is replaced by an even more uniform deposition.

Surface Patterning

Minireviews

Not chiral, but temporarily stereogenic: The introduction of a diaryl(oxy)methyl group into chiral auxiliaries, catalysts, and dopants can be rewarding: As a temporary stereogenic unit, it has a beneficial effect in a variety of asymmetric syntheses and has helped a series of well-known, efficient, and reliable "work horses" to succeed.



Stereochemistry

For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Reviews

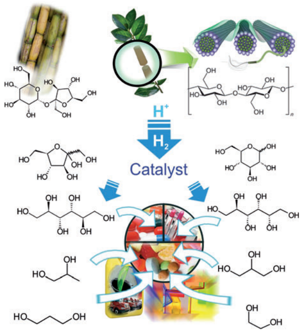
Renewable Feedstocks

A. M. Ruppert, K. Weinberg,
R. Palkovits* ______ **2564 – 2601**

Hydrogenolysis Goes Bio: From Carbohydrates and Sugar Alcohols to Platform Chemicals

Front Cover

Hydrogenolysis of renewable feedstocks allows direct access to valuable platform chemicals already integrated in today's value chains. Transformations based on hydrogenolysis bear the potential to bridge available technologies and future biorefinery concepts. This Review highlights developments in this field, with special emphasis on the direct transformation of cellulose and sugars.



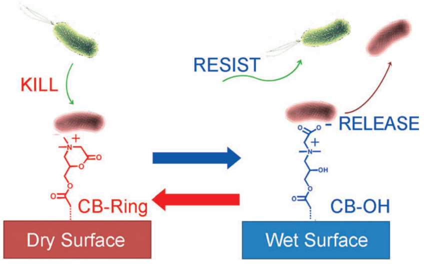
Communications

Smart Materials

Z. Cao, L. Mi, J. Mendiola,
J.-R. Ella-Menye, L. Zhang, H. Xue,
S. Jiang* ______ **2602 – 2605**

Reversibly Switching the Function of a Surface between Attacking and Defending against Bacteria

Frontispiece



Attack or defend! A smart polymer surface has two reversibly switchable equilibrium states, a cationic *N*,*N*-dimethyl-2-morpholinone (CB-Ring) and a zwitterionic carboxy betaine (CB-OH). CB-Ring will kill bacteria upon contact under dry conditions, whereas CB-OH will release the previously attached and dead bacteria and further resist adhesion of bacteria under wet conditions.

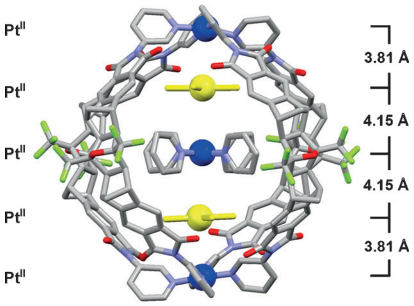
Metal Stacking

G. H. Clever,* W. Kawamura, S. Tashiro,
M. Shiro, M. Shionoya* ______ **2606 – 2609**

Stacked Platinum Complexes of the Magnus' Salt Type Inside a Coordination Cage

Inside Cover

Neatly wrapped up: Alternately stacked square-planar platinum(II) complexes inside a dinuclear coordination cage were prepared to give a discrete and soluble Pt_5-array of the Magnus' salt type. Characterization of the complex in solution was complemented by an X-ray crystal structure of $\{[Pt(pyridine)_4]\cdot[PtCl_4]_2@Cage\}$; this structure showed the linear, pentanuclear array within the cages and their circular packing into a hollow tubular superstructure.



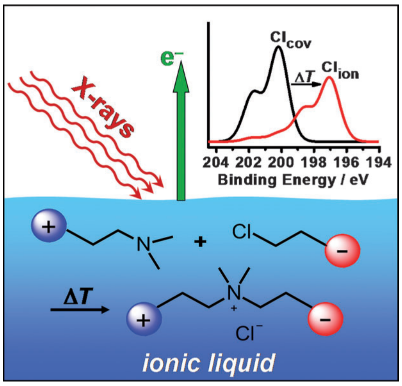
Ionic Liquids

VIP

C. Kolbeck, I. Niedermaier, N. Taccardi,
P. S. Schulz, F. Maier, P. Wasserscheid,
H.-P. Steinrück* ______ **2610 – 2613**

Monitoring of Liquid-Phase Organic Reactions by Photoelectron Spectroscopy

Inside Back Cover



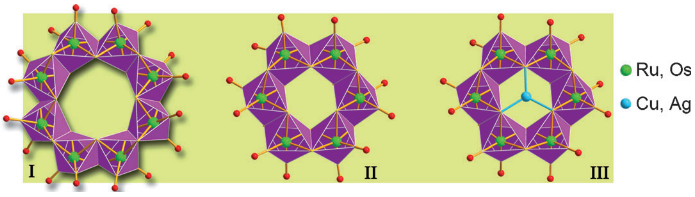
There are strings attached: After linking the reacting groups to head groups of ionic liquids to drastically lower the vapour pressures of the reactants, ordinary liquid-phase organic reactions can be monitored by in situ X-ray photoelectron spectroscopy. This approach is demonstrated for the nucleophilic substitution of an alkyl amine and an alkyl chloride moiety, which are attached to the cation and anion of ionic liquids, respectively.

Multinuclear Structures

S. L.-F. Chan, L. Shek, J.-S. Huang, S. S.-Y. Chui, R. W.-Y. Sun, C.-M. Che* ______ 2614 – 2617

Molecular Wheels of Ruthenium and Osmium with Bridging Chalcogenolate Ligands: Edge-Shared-Octahedron Structures and Metal-Ion Binding

Back Cover

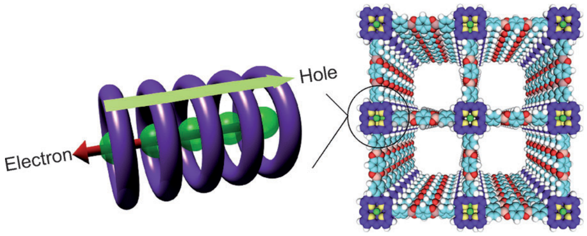


Inventing new wheels: Reaction of $[M_3(CO)_{12}]$ (M = Ru, Os) with 4-RC_6H_4SH afforded $[\{M(S\text{-}4\text{-}RC_6H_4)_2(CO)_2\}_8]$ (R = H; **I**) or $[\{M(S\text{-}4\text{-}RC_6H_4)_2(CO)_2\}_6]$ (R = Me, *i*Pr; **II**; see scheme), all of which have been structurally characterized. The octamers **I** are unique metal molecular wheels featuring skew-edge-shared octahedra with a central planar M_8 octagon. $[\{Ru(S\text{-}4\text{-}iPrC_6H_4)_2(CO)_2\}_6]$ selectively binds a Cu^+ or Ag^+ ion to form $[M'\{Ru(S(4\text{-}iPr\text{-}C_6H_4))_2(CO)_2\}_6]^+$ (**III**).

Conducting Materials

X. Feng, L. Liu, Y. Honsho, A. Saeki, S. Seki, S. Irle,* Y. Dong, A. Nagai, D. Jiang* ______ 2618 – 2622

High-Rate Charge-Carrier Transport in Porphyrin Covalent Organic Frameworks: Switching from Hole to Electron to Ambipolar Conduction

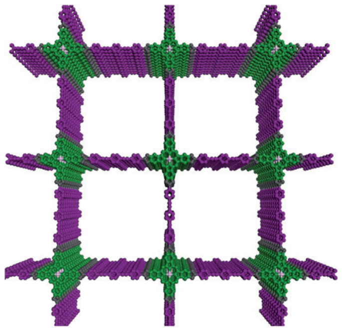


Well conducted: A two-dimensional porphyrin covalent organic framework is described. Owing to the eclipsed stacking alignment, the framework is conductive and allows high-rate carrier transport through the porphyrin columns (see picture). The central metal in the porphyrin rings changes the conducting nature of the material from hole to electron, and to ambipolar conduction. It also drives the high on–off ratio photoconductivity of the framework.

Covalent Organic Frameworks

E. L. Spitler, J. W. Colson, F. J. Uribe-Romo, A. R. Woll, M. R. Giovino, A. Saldivar, W. R. Dichtel* ______ 2623 – 2627

Lattice Expansion of Highly Oriented 2D Phthalocyanine Covalent Organic Framework Films



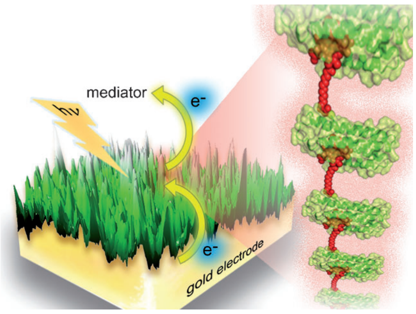
Diagonal Pore Width from 2.7-4.4 nm

Expanding into application: Covalent organic framework (COF) films are ideally suited for vertical charge transport and serve as precursors of ordered heterojunctions. Their pores, however, were previously too small to accommodate continuous networks of complementary electron acceptors. Four phthalocyanine COFs with increased pore size well into the mesoporous regime are now described (see picture).

Protein Assemblies

A. Onoda, Y. Kakikura, T. Uematsu, S. Kuwabata, T. Hayashi* ______ 2628 – 2631

Photocurrent Generation from Hierarchical Zinc-Substituted Hemoprotein Assemblies Immobilized on a Gold Electrode

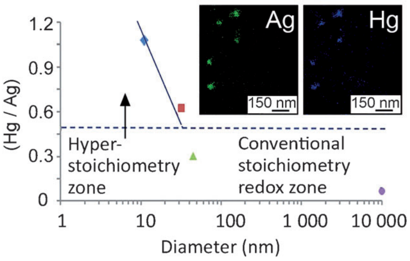


All connected: A protein-immobilized electrode comprising hierarchical assemblies of photoactive cytochrome b_{562} reconstituted with zinc protoporphyrin IX exhibits remarkably enhanced photocurrent generation relative to an electrode bearing a single zinc-substituted hemoprotein layer. The protein oligomers, which bear a covalently linked protoporphyrin group, assemble by a supramolecular heme/heme pocket interaction.

Nanoscale Chemistry

K. V. Katok, R. L. D. Whitby,* T. Fukuda,
T. Maekawa, I. Bezverkhyy,
S. V. Mikhalovsky,
A. B. Cundy ______ **2632 – 2635**

Hyperstoichiometric Interaction Between Silver and Mercury at the Nanoscale

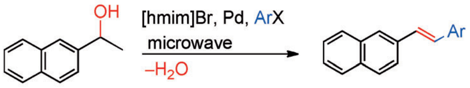


Breaking through the stoichiometry barrier: As the diameter of silver particles is decreased below a critical size of 32 nm, the molar ratio of aqueous Hg^{II} to Ag^0 drastically increases beyond the conventional Hg/Ag ratio of 0.5:1, leading to hyperstoichiometry with a maximum ratio of 1.125:1 (see figure). Therein, around 99% of the initial silver is retained to rapidly form a solid amalgam with reduced mercury.

Cross-Coupling

R. Kumar, A. Shard, R. Bharti, Y. Thopate,
A. K. Sinha* ______ **2636 – 2639**

Palladium-Catalyzed Dehydrative Heck Olefination of Secondary Aryl Alcohols in Ionic Liquids: Towards a Waste-Free Strategy for Tandem Synthesis of Stilbenoids

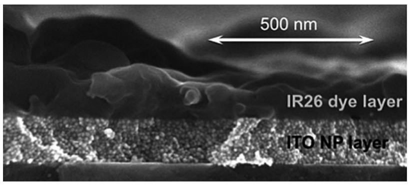


All in one: A tandem strategy has been developed wherein secondary aryl alcohols are directly coupled with aryl halides to provide stilbenoids through a dehydrative Heck sequence in the ionic liquid [hmim]Br, and with water as a by-product under microwave irradiation (see scheme). Classical methods do not permit this sequence to proceed in one pot, and some methods require multiple steps. hmim = 1-*n*-hexyl-3-methylimidazolium.

Surface Chemistry

A. Furube,* T. Yoshinaga, M. Kanehara,*
M. Eguchi, T. Teranishi* ______ **2640 – 2642**

Electric-Field Enhancement Inducing Near-Infrared Two-Photon Absorption in an Indium–Tin Oxide Nanoparticle Film



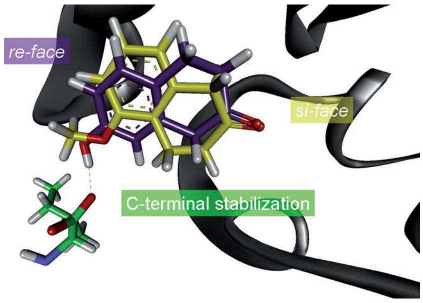
An enhancing factor: The enhancement of the electric properties of a dye molecule (IR26) by indium–tin oxide nanoparticles (ITO NPs, see picture) has been shown by measuring the near-infrared two-photon-excited transient absorption spectra. The dye molecule was excited much more efficiently in the presence of an ITO NP layer.

Enzyme Catalysis

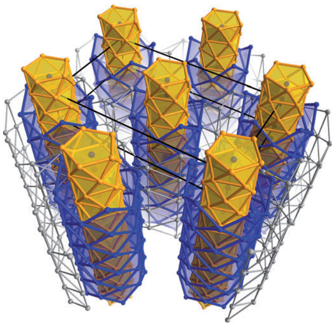
M. A. Schätzle, S. Flemming,
S. M. Husain, M. Richter, S. Günther,
M. Müller* ______ **2643 – 2646**

Tetrahydroxynaphthalene Reductase: Catalytic Properties of an Enzyme Involved in Reductive Asymmetric Naphthol Dearomatization

In reduced circumstances: Tetrahydroxynaphthalene reductase shows a broad substrate range including alternate phenolic compounds and cyclic ketones. Structural modeling reveals major enzyme–substrate interactions; C-terminal truncation of the enzyme causes an altered substrate preference, in accordance with stabilization of the substrate by the C-terminal carboxylate (see picture). This effect allows the identification of a homologous enzyme.



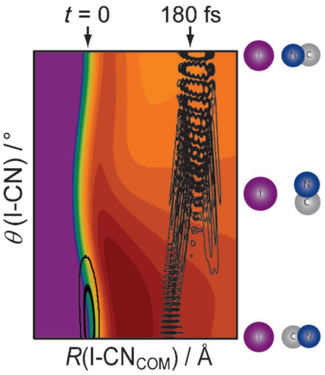
Solid-State Structures



Not quasi-crystalline: Approximate five-fold symmetry appears in bronze-type Cu–Sn rods that are separated by Na atoms in Na$_{2.8}$Cu$_5$Sn$_{5.6}$ (see picture). The rods are compared to the $[Sn@Cu_{12}@Sn_{20}]^{12-}$ cluster in the recently characterized $A_{12}Cu_{12}Sn_{21}$ phases (A = Na–Cs), and a saltlike description in analogy to Zintl phases of p-block metals is introduced for these new polar intermetallic phases with a high d-block metal content.

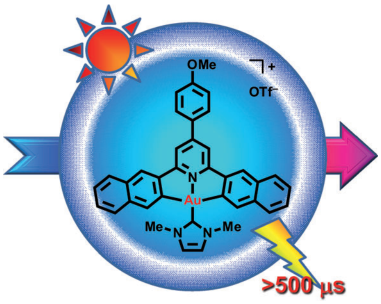
Energy Transfer

VIP



In a spin: The dynamics of photoexcited ICN$^-$(Ar)$_{0-5}$ are presented. Photodetachment produces quasi-thermal electron emission that leaves ICN with up to 2.85 eV of internal energy. Photodissociation at 2.5 eV leads to one-atom caging and highly solvated anion products. Calculations indicate efficient energy transfer into CN rotation upon excitation to the $^2\Pi_{1/2}$ excited state. CN rotation is vital to explain the unique dynamics observed.

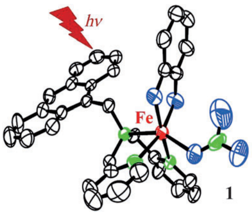
Organogold(III) Photochemistry



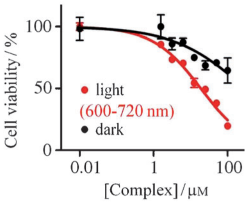
All that glitters is gold: Highly phosphorescent gold(III) complexes (see picture) with extended π-conjugated cyclometalating ligands exhibit rich photophysical and photochemical properties. They act as efficient photocatalysts/photosensitizers for oxidative functionalizations of secondary and tertiary benzylic amines and homogeneous hydrogen production from a water/acetonitrile mixture.

Bioinorganic Chemistry

VIP



1

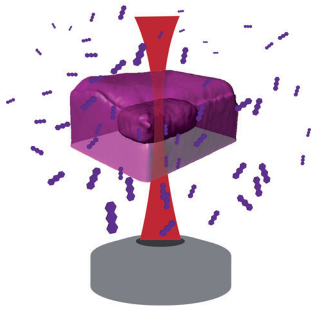


A red light for cancer cells: An iron(III) complex (**1**, see picture) that contains an anthracenyl fluorophore moiety and a catecholate ligand is a potent, metal-based PDT agent that efficiently photocleaves DNA in near-infrared light, has significant nuclear uptake, and high photocytotoxicity in red light by an apoptotic pathway in HeLa and MCF-7 cancer cells.

Metal–Organic Frameworks

S. Han, T. M. Hermans, P. E. Fuller, Y. Wei, B. A. Grzybowski* ________ **2662 – 2666**

Transport into Metal–Organic Frameworks from Solution Is Not Purely Diffusive

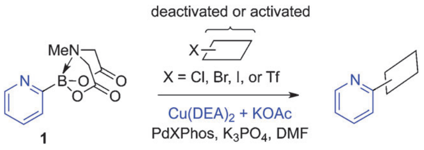


Chemistry in motion: A combination of confocal microscopy (see picture) and reaction-diffusion modeling provided a powerful toolkit with which solution transport into metal–organic framework crystals was studied. Commonly used pure diffusion models are insufficient to describe this process and, instead, it is necessary to account for the interactions of the guest molecules and the MOF scaffold.

Cross-Coupling

G. R. Dick, E. M. Woerly, M. D. Burke* ________ **2667 – 2672**

A General Solution for the 2-Pyridyl Problem

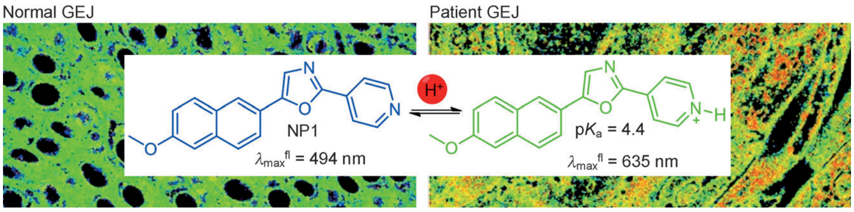


Problem solved: An air-stable 2-pyridyl borane that can effectively couple to a wide range of aryl and heteroaryl halides and pseudohalides has evaded the synthesis community for decades. The discovery that Cu(DEA)$_2$ powerfully enables palladium-mediated cross-couplings with air-stable boronates **1** has finally provided a general solution to this problem. DEA = diethanolamine, DMF = *N*,*N*′-dimethylformamide, Tf = trifluoromethanesulfonyl.

Fluorescent Probes

H. J. Park, C. S. Lim, E. S. Kim, J. H. Han, T. H. Lee, H. J. Chun, B. R. Cho* ________ **2673 – 2676**

Measurement of pH Values in Human Tissues by Two-Photon Microscopy



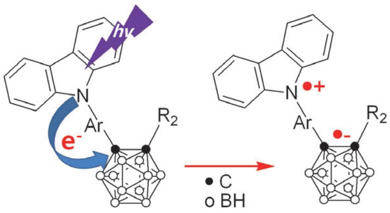
pH values go live! A ratiometric two-photon (TP) probe (NP1, see scheme) that has a significant TP action cross-section, high photostability, negligible toxicity, and can estimate pH values in live cells and human tissues by two-photon microscopy is described. NP1 can detect the difference in pH between live cells from the gastroesophageal junction (GEJ) and the lower esophageal sphincter of patients with and without esophagitis (see image).

Carborane Clusters

K.-R. Wee, W.-S. Han, D. W. Cho, S. Kwon, C. Pac,* S. O. Kang* ______ **2677 – 2680**

Carborane Photochemistry Triggered by Aryl Substitution: Carborane-Based Dyads with Phenyl Carbazoles

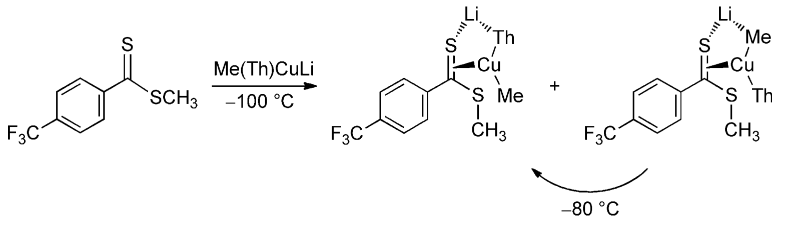
A bright combination: A new type of donor–acceptor dyad, carbazolylaryl-substituted *ortho*-carboranes, which are conveniently prepared from the corresponding acetylenes and decaborane pathways, showed unique excited-state behavior associated with electron transfer unlike the *meta*- and *para*-counterparts (see picture).



Organocuprates

S. H. Bertz,* R. A. Hardin, M. D. Murphy,
C. A. Ogle,* J. D. Richter,
A. A. Thomas ———— **2681 – 2685**

Minimization of Organocuprate Complexity through Self-Organization: Remarkable Orientation Effect in Mixed Cuprate π Complexes

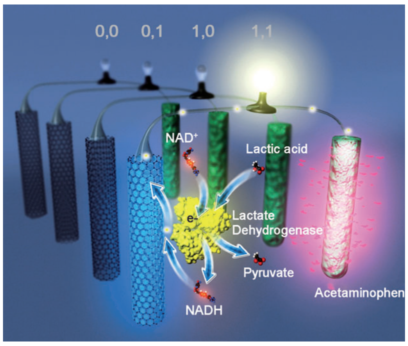


They “know” where to go: A powerful orientation effect has been observed in complexes of mixed organocuprates [R_TR_{NT}CuLi] and substrates with C=C, C=N, and C=S double bonds (see scheme; Th = thienyl). The preferred geometry of the intermediate complex sets up the facile addition of R_T to the double bond, rather than addition of the “dummy ligand”, R_{NT}.

Bioelectronic Devices

M. Zhou, N. Zhou, F. Kuralay,
J. R. Windmiller, S. Parkhomovsky,
G. Valdés-Ramírez, E. Katz,
J. Wang* ———— **2686 – 2689**

A Self-Powered “Sense-Act-Treat” System that is Based on a Biofuel Cell and Controlled by Boolean Logic

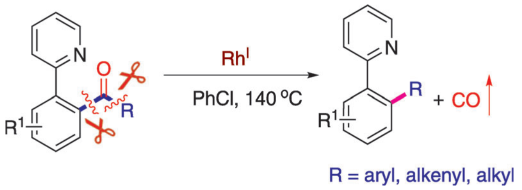


Bio-logic-al: An autonomous, integrated “sense-act-treat” system that is based on an enzymatic biofuel cell has been developed. The system couples a biocomputing logic-detection method with a drug-release system to provide a logic-activated therapeutic intervention in response to a simulated abnormal physiological state, without the need for an external power source, control electronics, or microelectromechanical actuators.

Biaryls

Z.-Q. Lei, H. Li, Y. Li, X.-S. Zhang, K. Chen,
X. Wang, J. Sun,* Z.-J. Shi* **2690 – 2694**

Extrusion of CO from Aryl Ketones: Rhodium(I)-Catalyzed C–C Bond Cleavage Directed by a Pyridine Group

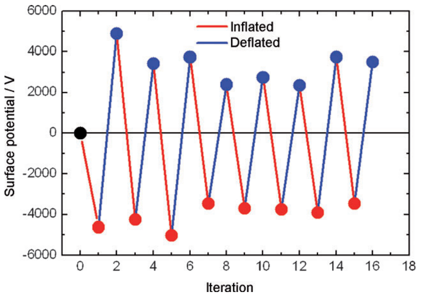


Snipping tool: The rhodium(I)-catalyzed extrusion of carbon monoxide from biaryl ketones and alkyl/alkenyl aryl ketones was developed to produce biaryls and alkyl/alkenyl arenes, respectively, in high yields (see scheme). A wide range of functionalities are tolerated. Not only does this method provide an alternative pathway to construct useful scaffolds, but also offers a new strategy for C–C bond activation.

Contact Electrification

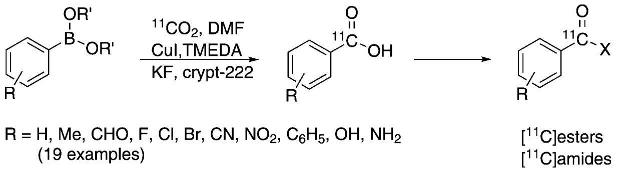
M. Sow, R. Widenor, A. Kumar, S. W. Lee,
D. J. Lacks,*
R. M. Sankaran* ———— **2695 – 2697**

Strain-Induced Reversal of Charge Transfer in Contact Electrification



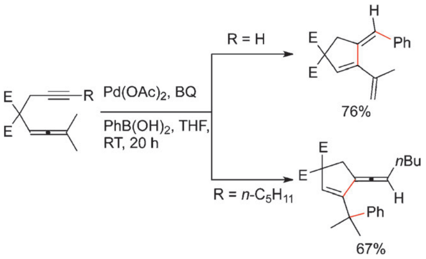
We have contact! Material strain can have a dominating effect on contact electrification. When a deflated (relaxed) balloon is rubbed against teflon, the teflon surface charges positively, but when the same balloon is inflated (strained), the teflon surface charges negatively. This result illustrates that material strain can control contact electrification and alter the driving force of some (yet unknown) charge-transfer species.

Radiochemistry



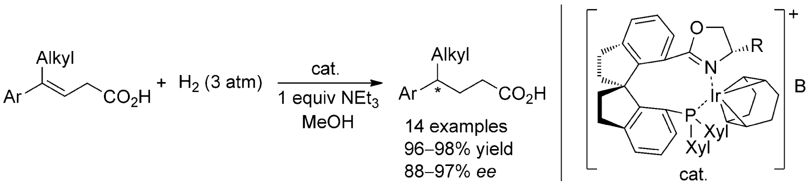
Rapid and direct: The carboxylation of boronic acid esters with $^{11}CO_2$ provides [^{11}C]carboxylic acids as a convenient entry into [^{11}C]esters and [^{11}C]amides (see scheme). This conversion of boronates is tolerant to diverse functional groups (e.g., halo, nitro, or carbonyl).

Carbocyclization



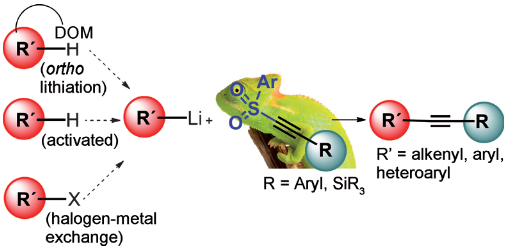
Vinylallenes or cross-conjugated trienes are obtained selectively in the title reaction (see scheme). Two possible mechanisms are suggested to rationalize the formation of the different types of products. Control experiments indicate that p-benzoquinone (BQ) plays an important role as a ligand in addition to its role as an oxidant. E = CO$_2$Me.

Asymmetric Hydrogenation

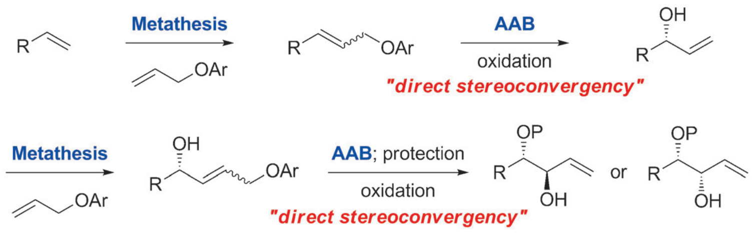


Chiral acids: A highly enantioselective iridium-catalyzed hydrogenation of β,γ-unsaturated carboxylic acids is developed for the preparation of chiral 4-alkyl-4-aryl butanoic acids (see scheme).

Synthetic Methods



Chameleon: A new strategy for the synthesis of a wide variety of alkynyl derivatives by the reaction of substituted arylsulfonylacetylenes with organolithium species is described (see scheme). The high yields, the simplicity of the experimental procedure, the broad scope of this reaction, and the formation of C$_{sp}$–C$_{sp^2}$ bonds without using transition metals are the main features of this methodology.

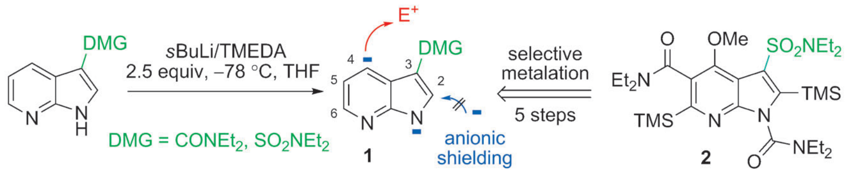


A copper-catalyzed asymmetric allylic boronation (AAB) gives access to *syn*- and *anti*-1,2-diols. The method facilitates an iterative strategy for the preparation of polyols (see scheme), such as the fully differentiated L-*ribo*-tetrol and protected D-*arabino*-tetrol. P=protecting group

Homogeneous Catalysis

J. K. Park, D. T. McQuade* **2717 – 2721**

Iterative Asymmetric Allylic Substitutions: *syn*- and *anti*-1,2-Diols through Catalyst Control

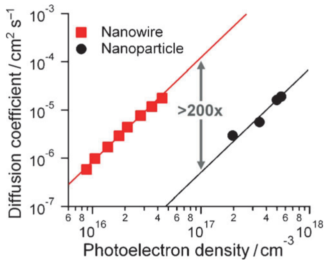


Strolling the ring: A general regioselective directed *peri*(C4)-metalation route to **1** through an in situ N-anionic protection of C2 is reported. The azaindoles may be elaborated by directed *ortho* metalation (DoM) and Suzuki coupling to more complex heterocyclic systems. An iterative ring-walk DoM sequence furnishes the exhaustively substituted **2**. DMG = directed metalation group, TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, TMS = trimethylsilyl.

Synthetic Methods

C. Schneider, E. David, A. A. Toutov,
V. Snieckus* **2722 – 2726**

In Situ Anionic Shielding for Regioselective Metalation: Directed *peri* and Iterative Metalation Routes to Polyfunctionalized 7-Azaindoles

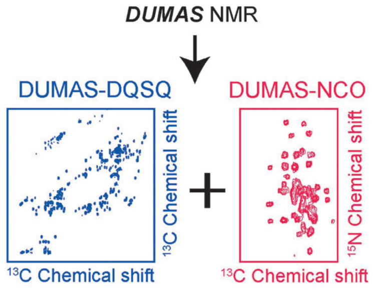


A rapid solvothermal approach was used to synthesize aligned 1D single-crystal rutile TiO_2 nanowire (NW) arrays on transparent conducting substrates as electrodes for dye-sensitized solar cells. The NW arrays showed a more than 200 times faster charge transport (see picture) and a factor four lower defect state density than conventional rutile nanoparticle films.

Solar Cells

X. Feng, K. Zhu, A. J. Frank, C. A. Grimes,
T. E. Mallouk* **2727 – 2730**

Rapid Charge Transport in Dye-Sensitized Solar Cells Made from Vertically Aligned Single-Crystal Rutile TiO_2 Nanowires



Fast data collection: A general method for dual data acquisition of multidimensional magic-angle spinning solid-state NMR experiments is presented (see picture). The method uses a simultaneous Hartmann–Hahn cross-polarization from ^1H to ^{13}C and ^{15}N nuclei and exploits the long-living ^{15}N polarization for parallel acquisition of two multidimensional experiments.

Solid-State NMR Spectroscopy

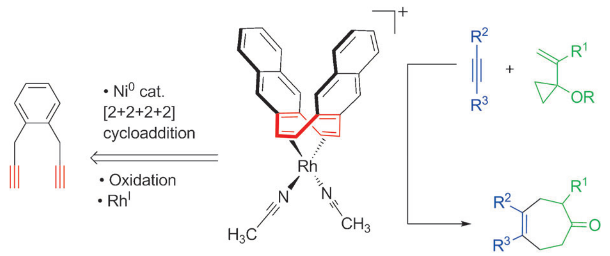
T. Gopinath, G. Veglia* **2731 – 2735**

Dual Acquisition Magic-Angle Spinning Solid-State NMR-Spectroscopy: Simultaneous Acquisition of Multidimensional Spectra of Biomacromolecules

Synthetic Methods

P. A. Wender,* A. B. Lesser,
L. E. Sirois **2736 – 2740**

Rhodium Dinaphthocyclooctatetraene Complexes: Synthesis, Characterization and Catalytic Activity in [5+2] Cycloadditions

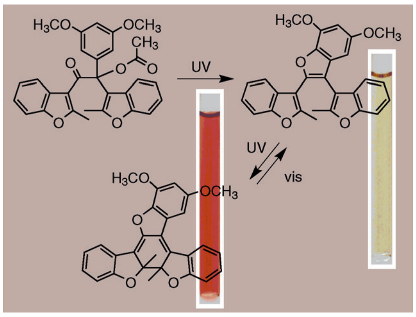


Rh COT in the act: A Ni^0-catalyzed [2+2+2+2] cycloaddition provides a high-yielding, scalable synthesis of the ligand dinaphtho[*a*,*e*]cyclooctatetraene (dnCOT). dnCOT complexation with Rh^I gives [Rh(dnCOT)(MeCN)$_2$]SbF$_6$ (see scheme), an excellent catalyst for [5+2] cycloadditions of vinylcyclopropanes and π-systems with impressive functional group compatibility.

Photochemistry

T. Wu, H. Tang, C. Bohne,*
N. R. Branda* **2741 – 2744**

Reporting the Release of Caged Species by a Combination of Two Sequential Photoreactions, a Molecular Switch, and One Color of Light

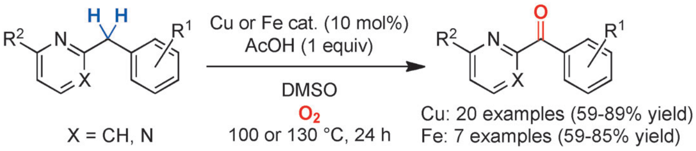


In the right light: UV light triggers bond breaking, liberates a caged carboxylic acid, and generates the central C=C double bond in the photoresponsive hexatriene molecule of a dithienylethene molecular switch. Light of the same wavelength converts the colorless isomer into its colored counterpart (see picture) in a visually convenient method to report on the success of the release event.

Synthetic Methods

J. De Houwer, K. Abbaspour Tehrani,
B. U. W. Maes* **2745 – 2748**

Synthesis of Aryl(di)azinyl Ketones through Copper- and Iron-catalyzed Oxidation of the Methylene Group of Aryl(di)azinylmethanes

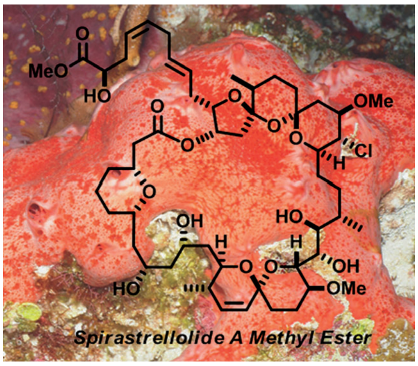


Sustainable Oxidations: An oxidation method to transform aryl(di)azinylmethanes into aryl(di)azinyl ketones is described. Base metals (copper and iron) as catalysts in combination with O$_2$ as the oxidant are used, which makes this method sustainable. The utility of this method is illustrated by the synthesis of 6-(4-methylbenzoyl)pyridine-2-carbaldehyde, which is an intermediate in the preparation of the drug Acrivastine.

Natural Product Synthesis

I. Paterson,* P. Maltas, S. M. Dalby,
J. H. Lim, E. A. Anderson **2749 – 2753**

A Second-Generation Total Synthesis of Spirastrellolide A Methyl Ester

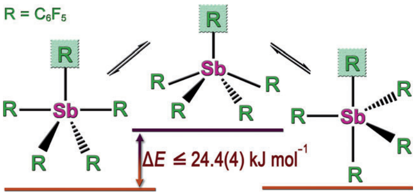


Marine macrolides: An improved second-generation total synthesis of the anticancer macrolide spirastrellolide A methyl ester has been achieved. The synthesis features a uniformly high level of stereocontrol combined with more expedient fragment assembly, and demonstrates a critical dependence of the crucial macrolactonization step on the substitution pattern of the C22–C24 linker region.

Organometallic Chemistry

M. A. García-Monforte, P. J. Alonso, I. Ara, B. Menjón,* P. Romero ____ **2754 – 2757**

Solid-State and Solution Structure of a Hypervalent AX_5 Compound: $Sb(C_6F_5)_5$



Eliminating restraints: A trigonal-bipyramidal structure has been found to be the energetically favored geometry of the hypervalent AX_5 molecule $Sb(C_6F_5)_5$ in the solid state and also in fluid solution, where molecules move freely and no crystal packing effects operate (see picture).

Heterocycles

A. E. Goetz, S. M. Bronner, J. D. Cisneros, J. M. Melamed, R. S. Paton,* K. N. Houk,* N. K. Garg* ____ **2758 – 2762**

An Efficient Computational Model to Predict the Synthetic Utility of Heterocyclic Arynes

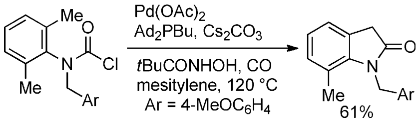
Think before you act: A computational approach is reported for evaluating the synthetic potential of heterocyclic arynes. Routine and rapid calculations of arene dehydrogenation energies and aryne angle distortion predict the likelihood that a given hetaryne can be generated, as well as the degree of regioselectivity expected in a reaction between a given hetaryne and a nucleophilic trapping agent (see picture).

Synthetic Methods

C. Tsukano, M. Okuno, Y. Takemoto* ____ **2763 – 2766**

Palladium-Catalyzed Amidation by Chemoselective $C(sp^3)-H$ Activation: Concise Route to Oxindoles Using a Carbamoyl Chloride Precursor

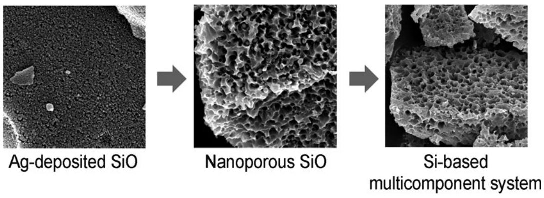
Quite select: A new strategy was developed for the synthesis of various oxindoles from carbamoyl chlorides. Under the optimum reaction conditions, with Ad_2PBu as a ligand, tBuCONHOH as an additive, and a CO atmosphere, selective $C(sp^3)-H$ activation proceeded in the presence of a $C(sp^2)-H$ bond. Ad = adamantyl.



Nanoporous Materials

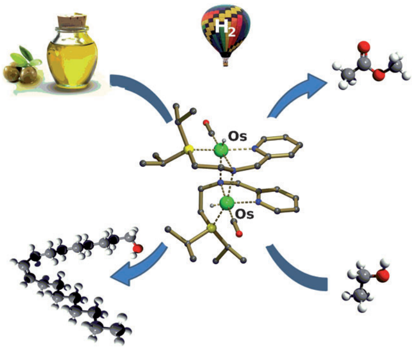
J.-I. Lee, K. T. Lee, J. Cho, J. Kim, N.-S. Choi,* S. Park* ____ **2767 – 2771**

Chemical-Assisted Thermal Disproportionation of Porous Silicon Monoxide into Silicon-Based Multicomponent Systems



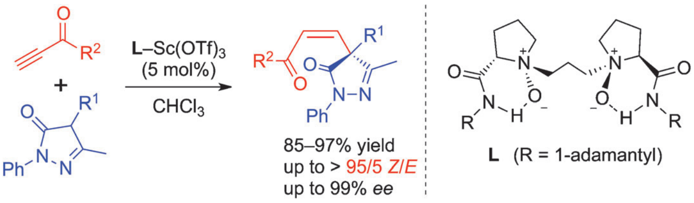
Under the surface: Ag nanoparticles are deposited onto the surface of commercially available SiO particles, and subsequent chemical etching results in the formation of nanoporous SiO (see picture) without changing the chemical and physical properties of the original SiO. Moreover, chemical-assisted thermal annealing produces a shape-preserving Si-based multicomponent system, which exhibits high-performance electrochemical properties.

Catalytic (De)Hydrogenation



There and back again: Hydrogenation of esters and the reverse reaction of dehydrogenative coupling of alcohols are efficiently catalyzed by dimeric complexes of Ru and Os under neutral conditions. The Os dimer (see picture) is an outstanding catalyst for the hydrogenation of alkenoates and triglycerides, and allows production of fatty alcohols from olive oil. This complex converts ethanol into ethyl acetate and hydrogen under reflux.

Asymmetric Synthesis



Highly selective: The title reaction is achieved with high enantiomeric and geometric control and thermodynamically unstable (*Z*)-enone derivatives are obtained as the major products (see scheme). The procedure tolerates a wide range of substrates to generate optically active pyrazolones with vinyl-substituted quaternary stereocenters.

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

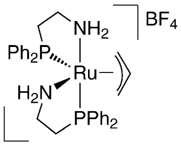
This article is available online free of charge (Open Access).

This article is accompanied by a cover picture (front or back cover, and inside or outside).

Service

Angewandte Corrigenda

Equation 2 of this Communication contains an incorrect chemical structure for **5**-major. The same mistake also occurs on page S8 of the Supporting Information. The correct structure is shown below.



5 (major)

A Highly Active Catalyst for the Hydrogenation of Amides to Alcohols and Amines

J. M. John,
S. H. Bergens* ________ **10377–10380**

Angew. Chem. Int. Ed. **2011**, *50*

DOI: 10.1002/anie.201103137

In this Communication, a reaction mechanism for the gasification of ethanol in supercritical water on a carbon-supported ruthenium catalyst was proposed based on the observed oscillations in product gas flow and composition (see page 6436). The authors have now become aware of an artifact in their experimental set-up, which made them realize that the published interpretation is not sufficiently supported by their experimental data.
Experiments that clarify the cause for the observed oscillations concerning the product gas are described in detail in the Supporting Information available for this Corrigendum. These experiments were performed by Marian Dreher in the authors' research group, who made them also aware of the artifact. He was co-supervised by Jörg Wambach. The authors thank both colleagues for their valuable contribution.
The authors wish to emphasize that all the information on the electronic state of the catalyst under hydrothermal and supercritical conditions, obtained from the XANES study, remains unaffected by this mistake.

Towards Understanding the Catalytic Reforming of Biomass in Supercritical Water

S. Rabe, M. Nachtegaal, T. Ulrich,
F. Vogel* ________ **6434–6437**

Angew. Chem. Int. Ed. **2010**, *49*

DOI: 10.1002/anie.201001660

The authors of this Communication wish to add an extra author:

Dr. Willem Schipper, Thermphos International B.V., Vlissingen (The Netherlands)

Dr. Schipper gave an important contribution to this article in terms of crucial discussion and interpretation of the preliminary electrochemical results and provided several important suggestions on how to characterize the otherwise elusive target compound.

Experimental Evidence of Phosphine Oxide Generation in Solution and Trapping by Ruthenium Complexes

D. Yakhvarov,* M. Caporali, L. Gonsalvi,
S. Latypov, V. Mirabello, I. Rizvanov,
O. Sinyashin, P. Stoppioni,
M. Peruzzini* ________ **5370–5373**

Angew. Chem. Int. Ed. **2011**, *50*

DOI: 10.1002/anie.201100822